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- (71) Applicant (for all designated States except US): CENTRAL RESEARCH LABORATORIES LTD. [GB/GB]; Dawley Road, Hayes, Middlesex UB3 1HH (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): DODGSON, John, Robert [GB/GB]; 71 Ballards Way, Croydon Surrey, CR2 7JP (GB). AUSTIN, Malcolm, Trayton [GB/GB]; 6 Moray Avenue, Hayes, Middlesex UB3 2AU (GB). SHAW, John, Edward, Andrew [GB/GB]; 45 Colne Avenue, West Drayton, Middlesex UB7 7AL (GB).

(74) Agent: WALKER, Neville, Daniel, Alan; QED I.P. Services Limited, Dawley Road, Hayes, Middlesex UB3 1HH (GB).

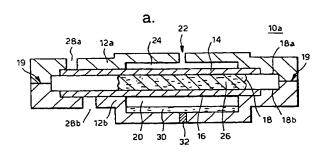
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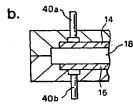
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(57) Abstract: The invention relates to a gas sensor and its method of manufacture. Previously gas sensors required a wick in order to maintain an electrode in a wetted state. This entailed complex structures and fabrication techniques. In a preferred embodiment a gas sensor has at least first and second sensing electrodes formed on a gas permeable substrate, at least one of the electrodes contacts a liquid electrolyte. There is also provided two self test electrodes, at least one of which is formed on the same surface of the substrate on which the sensing electrode is formed. A hydrophobic envelope surrounds a volume of solid polymer electrolyte, which defines an electrical pathway between the first and second self test electrodes thereby defining a self test gas generator. The invention thereby removes the need for wicks simultaneously in contact with an electrode and a liquid electrolyte.

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## A GAS SENSOR AND ITS METHOD OF MANUFACTURE

5 The present invention relates to a gas sensor and its method of manufacture. It relates particularly, but not exclusively, to a gas sensor for detecting carbon monoxide.

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Electrochemical gas sensors typically comprise two electrodes in contact with an electrolyte. Usually a liquid electrolyte is used, the electrolyte being kept in contact with one or more of the electrodes by means of a wick. An electrochemical gas cell which utilises liquid electrolyte is described in US Patent US-A-4100048 (Pompei et al). Here, a polarographic cell having thin film metal electrodes supported on a solid, rigid matrix, which acts as a wick, is disclosed. A liquid electrolyte is partially absorbed into the rigid matrix, the pores of the matrix define reaction sites between the gas, the electrodes and the electrolyte. The reaction area of this cell is low compared with sensor cells which use porous gas diffusion electrodes. This means that the polarographic cell may have a shorter life due to poisoning. The cell is also unsuitable for mass production techniques, as the electrodes are deposited, rather than screen printed, onto the matrix.

- In an alternative embodiment of a gas sensor a highly viscous or solid electrolyte is used, in which case no wick is required. Examples of gas sensors incorporating a solid electrolyte are disclosed in US Patents US-A-4820386 (LaConti and Griffith) and US-A-4900405 (Otagawa and Madou).
- LaConti and Griffith use a sheet of solid polymer electrolyte (SPE) with electrodes placed on either side of this sheet. A humidifying reservoir is also included in the sensor. The humidifying reservoir contains a liquid to keep the solid electrolyte wet. Otagawa and Madou use a planar array of electrodes with a layer of SPE cast over the electrodes. Gas reaches the electrodes either through the SPE film, or at the interface between the SPE film and parts of the electrodes projecting above the film.

The LaConti and Griffith gas sensor employs an SPE membrane with electrodes separately fabricated and pressed onto the membrane. The fabrication of this sensor is a complex process, and the polymer membrane and electrodes are also relatively

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expensive. An additional disadvantage of this sensor is that heat treatment of the SPE membrane is not possible as it tends to decompose. This limits the way in which the electrodes can be mounted on the membrane. During fabrication electrodes are pressed onto the polymer membrane, and are urged into contact, for example, by the cell housing structure or by cold welding of the electrode and the membrane. The design of the gas sensor also means that the electrodes must be contacted using expensive noble metals.

The Otagawa gas sensor requires only a relatively small amount of SPE, but the area of electrode available for gas reaction is small. Therefore, unless complex fabrication procedures are used, the cell output will be low and problems with short life through poisoning tend to occur.

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An aim of the present invention is to provide a gas sensor with a simpler structure than existing gas sensors, and a gas sensor that is simpler and cheaper to manufacture than existing gas sensors.

According to a first aspect of the invention there is provided a method of manufacturing a gas sensor, the method including the steps of: a) forming at least first and second electrodes on a substantially planar porous substrate, the substrate having a first major surface, and a second major surface; b) introducing a first electrolyte into at least a portion of the substrate, said first electrolyte being solid and defining a conductive path between the electrodes; c) providing a housing containing a reservoir, which, in use receives a second electrolyte; said second electrolyte maintaining the first electrolyte in a wetted state and d) bonding the substrate to the housing.

The first electrolyte preferably contains a polymer and may be introduced into the substrate in liquid form, or as a melted solid. Such an electrolyte is hereinafter referred to as a polymer electrolyte. Alternatively the first electrolyte is in the form of a solution, when it is applied, so that, upon evaporation of the solvent, the electrolyte is deposited in the substrate. The polymer electrolyte preferably has a high concentration of attached acid groups and which therefore conducts hydrogen ions such as, for example, Nafion<sup>TM</sup> produced by Dupont.

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Preferably the substrate has an open-cell structure, thus ensuring that gas may pass through the substrate to reach the electrodes. The first electrolyte may be introduced into, and supported by, the substrate.

Use of a porous substrate to contain the first electrolyte also allows the electrodes to be formed on the substrate in a rapid, efficient manner. The electrodes may then, for example, be sintered to the substrate to give a robust structure. This permits the electrode material to be taken through the region where the housing and substrate are bonded (the seal) to form external electrical contacts. The use of electrode material as electrical contacts means that the use of expensive noble metal contacts is avoided.

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The first electrolyte may be introduced into the substrate via the first major surface of the substrate and/or via the electrode(s) (if any) formed thereon. It is also possible to introduce the first electrolyte into the substrate via the second major surface of the substrate and/or via the electrode(s) (if any) formed thereon.

The housing is preferably a two-part housing comprising a first housing portion and a second housing portion. Preferably the substrate is disposed between the first housing portion and the second housing portion, the second housing portion containing the reservoir into which the second electrolyte is introduced. The second electrolyte is preferably aqueous electrolyte, and most preferably a hygroscopic liquid (such as concentrated sulphuric acid) so that there is a high relative humidity in the vicinity of the first electrolyte. This allows the first electrolyte to maintain a relatively constant conductivity, and removes the need for a wick.

Although electrodes are preferably sintered onto the substrate, they may be deposited onto the substrate by, for example, screen printing; filtering in selected areas from a suspension placed onto the substrate; by spray coating, or any other method suitable for producing a patterned deposition of solid material onto a substrate. Deposition might be of a single material or more than one material in layers so as, for example, to vary the properties of the electrode material through its thickness, or to add a second layer of increased electrical conductivity above or below the layer which is the main site of gas reaction.

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The first electrode may be formed on the first or second major surface of the substrate. The second electrode may also be formed on the first or second major surface of the substrate.

Some, or all, of the electrodes may extend past the first and/or second housing portions so as to form electrical contacts. This may be achieved by having a substrate in the form of a disc which has a larger diameter than the first and/or second housing portions. Alternatively, pins, metal strips or wires, may be used to form the electrical contacts. Holes or apertures which extend from the external surfaces of the housing portions to the electrodes may be formed in the first and/or second housing portions. These enable external electrical connections to be made to the electrodes by way, for example of contact pins of clips.

Preferably the substrate is bonded to the housing portions by the application of heat and/or pressure. This has the advantage of causing impregnation of the electrode with the housing material to seal the electrode in the region of the electrical contact. Bonding may, however, be achieved using adhesives or ultrasonic bonding.

The porosity of the substrate may be modified in a region adjacent the first electrolyte. The porosity of the substrate may be modified by the application of pressure to the substrate, or by filling the required area with a material which is impermeable to the second electrolyte. Thus selected regions of the substrate can be sealed so that electrolyte from the electrolyte reservoir does not pass into region(s) of the sensor where it is not required.

An electrochemical device having an electrolyte impregnated membrane is disclosed in European Patent Application No. EP-A1-0 862 232 (Asahi). Here, a foam with a closed-cell structure is impregnated with a non-aqueous electrolytic liquid. The electrolyte remains in a liquid form as it is held within the cells of the foam. This type of impregnated foam is not suitable for use in gas sensors where the electrodes are made using a print and sinter process as the latter techniques involve very high temperatures, and the foam is liable to leak.

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According to a second aspect of the invention there is provided a gas sensor comprising: a housing within which there is located: at least first and second sensing electrodes formed on a gas permeable substrate, at least one of the sensing electrodes, in use, contacts a first electrolyte; and two self test electrodes, at least one of which is formed on the same surface of the substrate on which a sensing electrode is formed, a hydrophobic envelope surrounds a volume of solid polymer electrolyte, which solid polymer electrolyte defines an electrical pathway between the first and second self test electrodes thereby defining a self test gas generator.

The hydrophobic envelope may be defined in the gas permeable substrate by for example impregnating suitable regions of the substrate.

The first electrode is preferably the working or sensing electrode for carrying out the desired electrochemical reaction between the electrolyte and the incoming gas to be sensed. The second electrode is preferably the counter electrode required for performing a counterpart electrochemical reaction with oxygen, and for creating the required ionic and electronic flows through the electrolyte between the electrodes.

The gas sensor may also include a reference electrode.

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Preferably electrodes are porous so that they are partially permeable to the first and second electrolytes. The electrodes are preferably formed of a porous electrically conductive material containing PTFE or similar polymeric binder and particles of catalyst. The electrodes may optionally contain additional catalyst support material, and also material to enhance conductivity. The catalyst may comprise, for example, ruthenium dioxide or platinum.

The electrodes are preferably operated by way of a potentiostat circuit. Such circuits are well-known in the art.

The housing may have a diffusion barrier in the form of a small aperture through which ambient gases can diffuse to contact the sensing electrode. The housing may be composed of a material (such as a plastics material) which has a lower melting point than the substrate, so that if heat and pressure are applied to the housing through the substrate, housing material is forced upwards and impregnates the substrate thus

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forming a strong bond between the housing and the substrate. The bond may, if necessary, be cooled under pressure to prevent relaxation of the structure before the housing material solidifies.

Preferably the substrate includes a porous plastic such as, for example, a porous fluoropolymer such as PTFE, a glass fibre mat, or any other absorbent medium onto which electrodes can be deposited. This substrate is preferably permeable to gases, but impermeable to the second electrolyte.

A number of embodiments of the invention will now be described, by way of example only, with reference to the accompanying Figures, in which:-

Figure 1a shows a cross-sectional view of a first gas sensor;

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Figure 1b shows the first gas sensor having contact pins;

Figure 2 shows a cross-sectional view of a second gas sensor;

Figure 3 shows a cross-sectional view of a third gas sensor;

Figure 4a shows a cross-sectional view of a gas sensor having self-test capability; and

Figure 4b shows a plan view of the gas sensor of Figure 4a.

Referring now to Figure 1, there is shown a generally circular gas sensor (10a) comprising a two-part housing (12a) and (12b), and sensing electrode (14) and counter electrode (16) formed on a porous membrane (18). Housing part (12b) is cylindrical with a hollow interior defining an electrolyte reservoir (20) for receiving liquid electrolyte (30). The housing parts (12a) and (12b) support the membrane (18), and also form an acid-tight seal so that electrolyte (30) cannot leak from the sensor assembly.

Housing part (12a) is a disc shaped cap member having an aperture (22) therein to permit atmospheric gas to diffuse to a recessed manifold area (24), and thence to sensing electrode (14). Aperture (22) may be in the form of a diffusion barrier to control the amount of gas reaching sensing electrode (14). Membrane (18) is disposed between housing parts (12a) and (12b) and is in the form of a disc. A portion of the membrane is impregnated with a solid polymer electrolyte (26). A hydrophobic perimeter surrounds

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the solid polymer electrolyte and prevents it from leaching into the electrolyte or into the from the membrane.

Electrodes (14) and (16) are formed of a mixture of electrically conductive catalyst particles in PTFE binder, and are sintered onto substrate (18). Sensing electrode (14) is formed on the upper surface of substrate (18), while counter electrode (16) is formed on the lower surface of the substrate and is in contact with electrolyte (30). Housing portions (12a) and (12b) have apertures (28a) and (28b) extending from the outer surface of the housing portions to the electrodes, so that external electrical contact may be made with respective electrodes (14) and (16). Apertures (28a) and (28b) are offset one from another in order that the assembly is not weakened.

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Solid polymer electrolyte (26) is kept partially wet by electrolyte (30). Electrolyte (30) is hygroscopic. Reservoir (20) is closed at the base by means of a base member (not shown) having a pressure relief aperture, or vent, (32) in order to allow equalisation of pressure across the substrate (18). Vent (32) is closed by a porous membrane.

A method of making an external electrical connection with gas sensor (10a) is shown in Figure 1b. Here, conductive contact pins (40a) and (40b) are mounted in housing portions (12a) and (12b) in order to make electrical connection with respective electrodes (14) and (16).

On operation of sensor (10a), gas from the environment passes through the diffusion barrier (22) to recessed manifold area (24). The diffusion barrier (22) controls the rate of arrival of atmospheric gas at sensing electrode (14). If the gas to be sensed is present, an electrochemical reaction is created at sensing electrode (14) on contact between the electrolyte and the gas. An electrochemical reaction also occurs at counter electrode (16) with oxygen from the atmosphere. Current is carried through the electrolyte by ions produced in the reactions, and by electrons in an external circuit. The current in the external circuit indicates the concentration of carbon monoxide in the atmosphere.

Referring now to Figure 2, there is shown a gas sensor (10b) comprising a two-part housing (12a) and (12b), and sensing electrode (14) and counter electrode (16) both formed on the upper side of substrate (18). As in the previous embodiment, lower

housing part (12b) is cylindrical with a hollow interior forming an electrolyte reservoir (20). Electrolyte reservoir (20) contains electrolyte (30). In this embodiment of the invention, electrolyte (30) is permitted to directly contact the region of the substrate (18) which is impregnated with SPE (26). Atmospheric gas is permitted to diffuse to recessed manifold area (24) via aperture (22), and thence to sensing electrode (14) only. Counter electrode (16) is covered by a portion of upper housing part (14a) so that gas from the atmosphere cannot directly diffuse thereto. As in the aforedescribed sensor (10a), substrate layer (18) is disposed between housing parts (12a) and (12b) and is in the form of a disc. Co-planar electrodes (16) and (18) extend past opposite sides of housing portion (12a) to form electrical contact regions (28a) and (28b).

In Figure 3 there is shown a further embodiment of the invention. Gas sensor (10c) also comprises a two-part housing (12a) and (12b), and sensing electrode (14) and counter electrode (16) formed on substrate (18). As in Figure 2, housing part (12a) permits atmospheric gas to diffuse to recessed manifold area (24), and thence to sensing electrode (14) only. However, in this embodiment of the invention, electrodes (14) and (16) are formed on the lower surface of substrate layer (18), so that gas from the atmosphere diffuses through the substrate (18) before reaching the electrodes. Electrodes (14,16) and the exposed lower surface of substrate layer (18) are coated with a layer of SPE (26). SPE layer (26) is kept wet by electrolyte (30) contained within electrolyte reservoir (20). In this embodiment of the invention, housing part (12a) is larger in diameter than housing part (12b) so that electrodes (14) and (16) extend past housing part (12b) to form respective electrical contact regions (28a) and (28b).

A gas sensor with self-test capability is shown in Figures 4a and 4b. Gas sensor (10d) comprises: 1) a two-part housing (12a) and (12b); 2) a sensor cell comprising sensing electrode (14), reference electrode (15) and a counter electrode (16) (common to both the sensor cell and the test cell) formed on the lower surface of substrate (18); and 3) a self-test cell (36). The self-test cell (36) includes a porous membrane or test-electrode (17), loaded with a volume of SPE, and a barrier region (34). Barrier region (34) is formed by filling the outer edges of region (26) with a hydrophobic polymer. Alternatively, the porosity of the outer edges of region (26) may be removed by, for

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example, compression. Barrier region (34) ensures that wicking of the electrolyte (20) from electrolyte reservoir (30) to recessed manifold area (24) does not occur.

Co-planar electrodes (14), (15) and (16) extend past opposite sides of housing portions (12a) and (12b) to form electrical contact regions (28a) (not shown), (28c) and (28b), respectively. Test-cell electrode (17) also extends beyond housing portion (12a) to form an electrical contact (28d). A wicking means (not shown) may be provided to keep the electrolyte (30) in contact with electrodes (14), (15), and (16).

The operation of the gas sensor (10d) will now be briefly described. During operation of the sensor in self-test mode, hydrogen gas is generated at generating electrode (17). The hydrogen gas passes through the substrate (18), via recessed manifold (24), to sensing electrode (14) where an electrochemical reaction occurs. This reaction produces a current indicative of the amount of hydrogen gas generated. The size of the current generated can be used to check whether the sensor is operating correctly. Hydrogen is prevented from reaching reference electrode (15) by, for example, sealing part of substrate (18) adjacent this electrode, or by the design of housing portion (12a). Oxygen is formed at common counter electrode (16) to complete the gas generation circuit. The polymer electrolyte (26) is kept hydrated by the presence of liquid electrolyte (30), while the current paths in the two cells are kept separate. The operation and structure of a gas sensor incorporating a self-test function is discussed more fully in International Patent Application No. WO-A1-9825139.

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The manufacture of gas sensors (10a) to (10d) will now be described. Firstly the electrodes are sintered (at a temperature of between 300°C and 370°C for approximately 1 hour) onto porous substrate (18). These conditions fuse the binder particles to the substrate. The polymer electrolyte (26) is then introduced into substrate (18) as a liquid. The liquid polymer wets the porous substrate (18), flows into the substrate, fills the porous areas, and then solidifies. The filling of the substrate might be complete or partial, depending on the properties of the chosen polymer and substrate. The liquid polymer flows a little way into the electrodes, up to the interface with the substrate. This ensures that good electrical contact with the electrodes is made, while still enabling gas to access the area of reaction at the interface between the electrodes and the SPE (26).

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In gas sensor (10a), the counter electrode is deposited on the lower surface of substrate (18). The electrode may be deposited on the substrate so that small holes are left in the electrode. The polymer electrolyte is then introduced into the substrate through the holes. Alternatively, the polymer electrolyte (26) may be introduced into substrate (18) through the electrodes (14, 16), or wicked through the side of the substrate.

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In gas sensor (10b) the polymer may be introduced through the opposite side of the substrate from the electrodes, i.e., the lower surface of substrate (18). Alternatively, the polymer electrolyte may be wicked through the side of the substrate.

In gas sensor (10c) the polymer (26) is introduced through the lower surface of substrate (18) – the surface of the substrate containing the electrodes (14, 16). However, it is only required to impregnate the region of the substrate in contact with the electrodes. This is achieved by using a polymer electrolyte (26) with a high viscosity, or by protecting a region of the substrate by first filling it with a substance which can later be removed while leaving the solidified electrolyte (26) in situ.

In gas sensor (10d), the polymer electrolyte (26) is introduced into substrate (18) in the same manner as for gas sensor (10a).

To assemble the structures shown in Figures 1 to 4, the SPE impregnated substrate is sandwiched between the housing parts (12a) and (12b). Heat and pressure are then applied to the peripheral parts of this structure in order to seal it. Electrolyte (30) is then introduced into reservoir (20) through a filling port (not shown) formed in lower housing portion (12b).

For sensor (10a), electrically conductive polymer may be positioned between the electrodes and the conductive contact pins (40a) and (40b), so that when heat and pressure are applied, the conductive polymer moulds itself around the heads of the contact pins and impregnates into-the electrode material, thereby creating a stable and secure electrical coupling.

The following advantages of the gas sensors described herein are:

- (1) The planar electrode assembly simplifies production of the sensor, as all electrodes can be produced in a single process;
- 5 (2) The electrical contact method avoids use of expensive metal contacts and forms contacts rapidly and simultaneously with the cell assembly process;
  - (3) The use of solid polymer electrolyte means that a wick is not required wicks complicate the design of gas sensors;
  - (4) The sealing process produces a high strength cell;
- (5) The small number of components and processes needed for assembly means that assembly is rapid and cheap. The components are individually robust and so damage during assembly is unlikely; and
  - (6) The cell assembly process is capable of automation.

Variation may be made to the aforementioned embodiments without departing from the scope of the invention.

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#### Claims

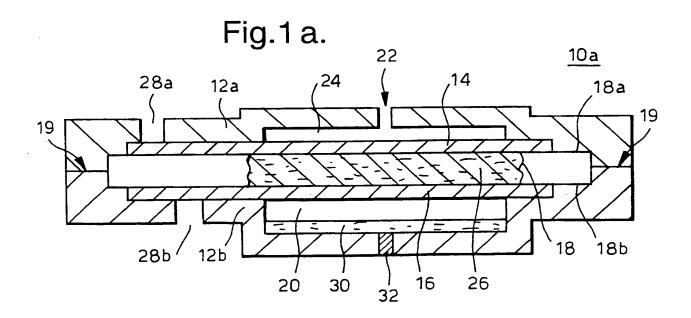
- 1. A method of manufacturing a gas sensor, the method including the steps of: a)

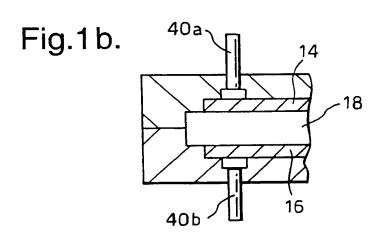
  forming at least first and second electrodes on a substantially planar porous substrate, the substrate having a first major surface, and a second major surface; b) introducing a first electrolyte into at least a portion of the substrate, said first electrolyte being solid and defining a conductive path between the electrodes; c) providing a housing containing a reservoir, which, in use receives a second electrolyte; said second electrolyte maintaining the first electrolyte in a wetted state and d) bonding the substrate to the housing.
  - 2. A method according to claim 1 including the step of introducing a second electrolyte (30) into the reservoir (20).
- 3. A method according to claims 1 or 2 wherein the electrodes (14,16) are sintered onto the substrate (18).
- 4. A method according to any preceding claim wherein the first electrode (14) is formed on the first major surface (18a) of the substrate.
  - 5. A method according to any of claims 1 to 3 wherein the first electrode (14) is formed on the second major surface (18b) of the substrate.
- 6. A method according to claim 5 wherein the second electrode (16) is formed on the first major surface (18a) of the substrate.
  - 7. A method according to any of claims 1 to 5 wherein the second electrode (16) is formed on the second major surface (18b) of the substrate.
  - 8. A method according to any preceding claim wherein the first electrolyte (26) is introduced into the substrate (18) in liquid form.
- 9. A method according to claim 8 wherein the first electrolyte (26) is introduced into the substrate (18) in the form of a solution.

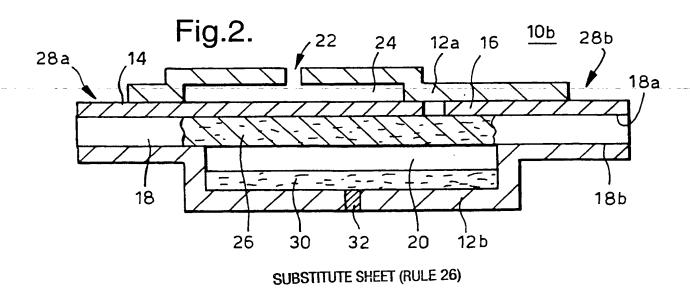
- 10. A method according to any preceding claim wherein the first electrolyte (26) is introduced into the substrate (18) via the first major surface (18a) of the substrate and/or electrodes (14,16) formed thereon.
- 5 11. A method according to any preceding claim wherein the first electrolyte (26) is introduced into the substrate via the second major surface (18b) of the substrate and/or electrodes (14,16) formed thereon.
- 12. A gas sensor (10) comprising: a housing within which there is located: at least first and second sensing electrodes formed on a gas permeable substrate, at least one of the sensing electrodes, in use, contacts a first electrolyte; and two self test electrodes, at least one of which is formed on the same surface of the substrate on which a sensing electrode is formed, a hydrophobic envelope surrounds a volume of solid polymer electrolyte, which solid polymer electrolyte defines an electrical pathway between the first and second self test electrodes thereby defining a self test gas generator.
  - 13. A gas sensor (10) according to claim 12 wherein the second electrode (16) is a counter electrode.
- 20 14. A gas sensor (10) according to any of claims 12 or 13 further including a reference electrode (15).

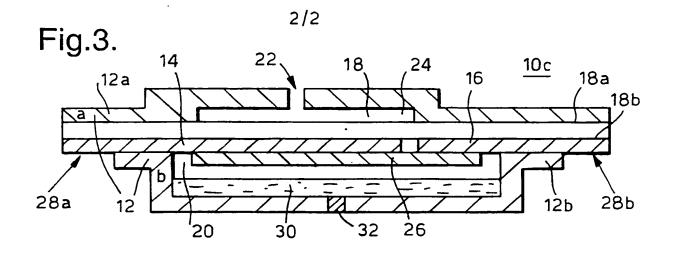
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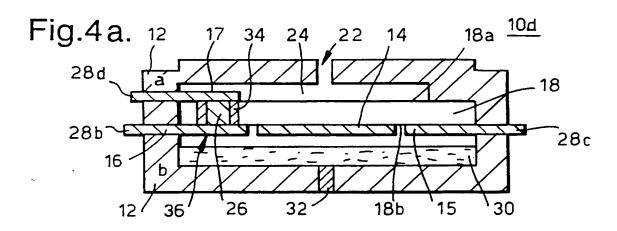
- 15. A gas sensor (10) according to any of claims 12 to 14 further including a test-cell (36) comprising a generation electrode (17) and a counter electrode (16).
- 16. A gas sensor (10) according to claim 16 wherein the counter electrode (16) is common to the test-cell (36) and the sensor.
- 17. A gas sensor (10) according to any of claims 12 to 17 wherein at least one of the electrodes (14,15,16,17) extends beyond the first (12a) and/or second (12b) housing portions so as to form electrical contacts (28a,28b,28c).
  - 18. A gas sensor and method of manufacture (10) substantially as described herein with reference to the Figures.

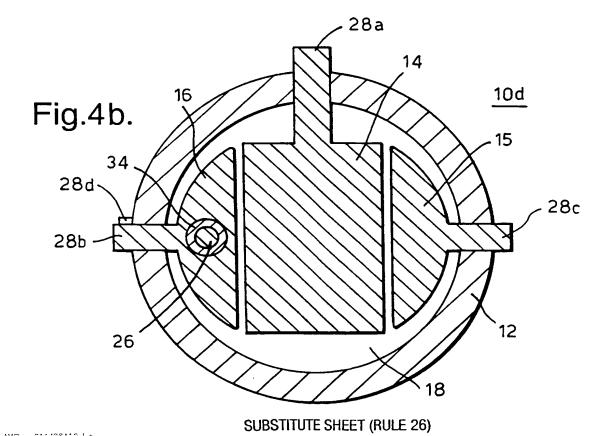












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- (71) Applicant (for all designated States except US): CENTRAL RESEARCH LABORATORIES LTD. [GB/GB]; Dawley Road, Hayes, Middlesex UB3 1HH (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): DODGSON, John, Robert [GB/GB]; 71 Ballards Way, Croydon Surrey, CR2 7JP (GB). AUSTIN, Malcolm, Trayton [GB/GB]; 6 Moray Avenue, Hayes, Middlesex UB3 2AU (GB). SHAW, John, Edward, Andrew [GB/GB]; 45 Colne Avenue, West Drayton, Middlesex UB7 7AL (GB).

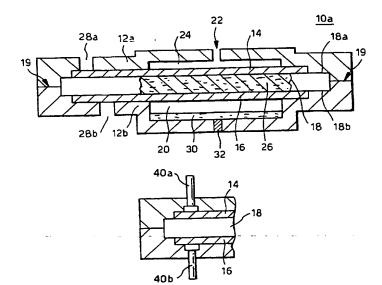
- (74) Agent: WALKER, Neville, Daniel, Alan; QED I.P. Services Limited, Dawley Road, Hayes, Middlesex UB3 1HH (GB).
- (81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
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[Continued on next page]

(54) Title: A GAS SENSOR AND ITS METHOD OF MANUFACTURE



(57) Abstract: The invention relates to a gas sensor and its method of manufacture. Previously gas sensors required a wick in order to maintain an electrode in a wetted state. This entailed complex structures and fabrication techniques. In a preferred embodiment a gas sensor has at least first and second sensing electrodes formed on a gas permeable substrate, at least one of the electrodes contacts a liquid electrolyte. There is also provided two self test electrodes, at least one of which is formed on the same surface of the substrate on which the sensing electrode is formed. A hydrophobic envelope surrounds a volume of solid polymer electrolyte, which defines an electrical pathway between the first and second self test electrodes thereby defining a self test gas generator. The invention thereby removes the need for wicks simultaneously in contact with an electrode and a liquid electrolyte.

11/14864 A3



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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Inter anal Application No PCT/GB 00/03285

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